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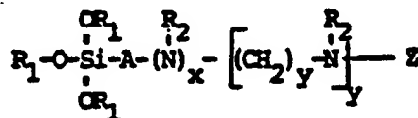
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(54) Polyimide coating composition.

(57) A polyimide coating composition comprising an homogeneous liquid solution of (a) a polyimide or polyimide precursor, (b) a substituted aminosilane compound and (c) aprotic solvent. The aminosilane compound corresponds to the structure:



polyimide + silane (amino)

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POLYIMIDE COATING COMPOSITION

Field of Invention

The invention is directed to polyimide coating compositions which form highly adherent films on various
5 substrates.

Background of the Invention

10 Polyimides find extensive use in electronic applications where they are useful in forming dielectric films on electrical and electronic devices such as capacitors and semiconductors. Typical uses for polyimides include protective coatings for semiconductors, dielectric layers for multilayer integrated circuits, high temperature solder masks, bonding multilayer circuits, final passivating coatings on electronic devices and the like.

15 It is well known in the polymer art to make thermally stable all-aromatic polyimides by the condensation polymerization of dianhydrides and diamines to form polyamic acid. Such polyimide precursors are disclosed inter alia in U.S. 3,179,634 to Edwards. Solutions of such polyamic acids in aprotic solvents are then coated on appropriate substrates and then dehydrated to the corresponding polyimides by heating at high temperatures, e.g., 300 to 400° C.

20 In each application the polyimide is applied as a liquid or in the form of its polyamic acid precursor which then must be cured by heating to form the polyimide. A typical high performance aromatic polyimide does not naturally adhere well to inorganic substrates, and areas having poor adhesion can become sites for later metal corrosion.

Heretofore, the problems of adhesion of polyimide or polyimide precursors to inorganic substrates were
25 approached mainly by applying a layer of adhesion promoter to the substrate which was capable of serving as a reaction site with the polyamic acid precursor of the polyimide. However, this involves an additional step in the already complex fabrication process for electronic components.

To avoid such an extra processing step, there have been attempts to incorporate adhesion promoters directly into the polyimide or polyamic acid coating solution. Aminosilane materials such as N-
30 (triethoxysilylpropyl)amino maleic acid have been used for this purpose. However, such one-step application systems frequently have the disadvantage that they require that the initial polymer cure be carried out at a temperature of 250 to 300° C in air to obtain adequate adhesion. It would therefore be highly advantageous to have a one-step system which would not require a high temperature cure in air, but can be carried out in a non-oxidizing atmosphere such as nitrogen or argon to reduce device metal oxidation.

35

Prior Art

40 U.S. 3,288,754, Green

The reference is directed to polyamide-polyimides containing organosilyl groups.

U.S. 4,200,724, Darms et al.

The reference is directed to polymeric adhesion promoters containing imidyl and silyl groups. The
45 reference discloses generally the use of various silanes to improve adhesion of fiber-reinforced plastics, lacquers and adhesives.

U.S. 4,306,073, Darms et al.

Monomeric, oligomeric and polymeric silicon-modified bis-phthalic acid derivatives are used as adhe-
50 sion promoters for resins.

U.S. 4,389,504, Clair et al.

The reference is directed to rubber-toughened polyamic acid adhesive compositions terminated with aromatic aminosilane groups.

U.S. 4,430,153, Gleason et al.

The reference is directed to converting the surface of aromatic polyimides to a silicon-containing alkyl polyamide-polyimide for the purpose of improving adhesion to inorganic substrates such as SiO₂, Si₃N₄ and aluminum.

U.S. 4,499,149, Berger

The reference discloses that the adhesive properties of polyamides are improved by incorporating a polysiloxane unit into the molecule.

U.S. 4,499,252, Igarashi et al.

The reference is directed to polyimide precursors having aminosilane groups incorporated into the polymer. The polymer is made by reacting a silane-modified polycarboxylic acid with a diamine.

U.S. 4,582,119, Darms et al.

The reference is directed to flexible printed circuits in which adhesion of the printed tracks is improved by coating one side of the printed foil with a layer of polyamide, polyimide or polyamide-imide containing siloxane groups.

U.S. 4,591,653, Kunimune et al.

The reference is directed to a silane-polyimide precursor which is the coreaction product of a silicone diamine with an aromatic tetracarboxylic acid anhydride and an aminosilicone compound.

U.S. 4,645,688, Makino et al.

The reference is directed to encapsulating materials which are comprised of polyamic acids obtained by reaction of a diaminosiloxane, an organic diamine and a tetracarboxylic acid dianhydride.

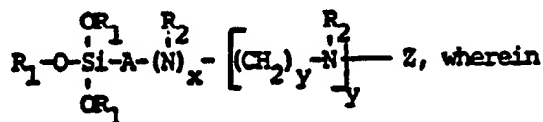
J58168624, Nitto (Assignee)

The reference is directed to screen printable pastes containing polyamic acids modified with diaminosiloxane. The pastes are said to form films having good adherence to substrates.

Summary of the Invention

The invention in its primary aspect is directed to a coating composition comprising an homogeneous liquid solution of:

- (a) polyimide or polyimide precursor;
- (b) an aminosilane compound corresponding to the structural formula:

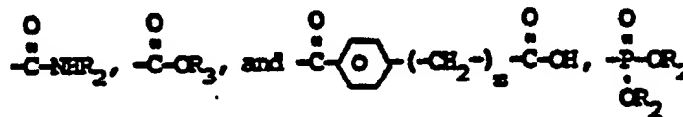


R₁ is independently selected from C₁₋₃ alkyl groups;

A is either phenylene or $-(CH_2)_w-$ in which w is an integer of from 1 to 6;

R₂ is independently selected from -H and C₁₋₃ alkyl groups;

Z is independently selected from -H, C₁₋₈ alkyl, C₇₋₁₂ alkaryl, C₇₋₁₂ aralkyl, glycidyl, aromatic carboxyl,



in which R₃ is phenyl or C₁₋₈ alkyl;

x is z or 1;

y is zero or an integer of from 1 to 3; and

z is zero or an integer of from 1 to 3;

the sum of the carbon atoms in moieties R₂ and Z being at least 3; and

- 5 (c) aprotic solvent, the weight ratio of (b) to (a) being from 0.01 to 0.2.

In a second aspect, the invention is directed to an inorganic substrate on which is mounted at least one semiconductor or other electronic device, which device is coated and/or encapsulated with a polymeric film which was formed by applying to the substrate and/or the device a coating of the above-described composition and then heating it to harden the coating by removal of solvent therefrom and/or by imidization.

10

Detailed Description of the Invention

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Aprotic Solvent:

The preparation of soluble polyimides and polyamic acid precursors of polyimides is carried out by condensation polymerization of dianhydrides and diamines in a aprotic solvent medium. Therefore, suitable
20 aprotic solvents for the method of the invention are N-methyl pyrrolidone, dimethylacetamide, dimethyl sulfoxide and dimethylformamide. N-methyl pyrrolidone is a particularly preferred solvent for use in the invention. Mixtures of the solvents can be used as well to adjust the volatility of the solvent medium. The solvent should, however, be substantially free of water. Solvents having a water content of no more than 0.1% wt. are preferred.

25

Polyimide or Polyimide Precursors:

It is well known in the polymer art to make thermally stable all-aromatic polyimide precursors by the
30 condensation polymerization of dianhydrides and diamines to form polyamic acid. Such polyimide precursors are disclosed inter alia in U.S. 3,179,634 to Edwards.

A wide variety of polyamic acids (polyimide precursors) and soluble polyimides can be used in the compositions of the invention such as the thermally stable aromatic polyimides disclosed in Edwards, U.S. 3,179,634 and by Fryd in U.S. 4,588,804 and the polyimides which are disclosed by Fryd and Merriman in
35 U.S. 4,533,574 and U.S. 4,562,100. Photopolymerizable polyimides such as those disclosed by Fryd and Goff in U.S. 4,551,522 are also useful for the practice of the invention.

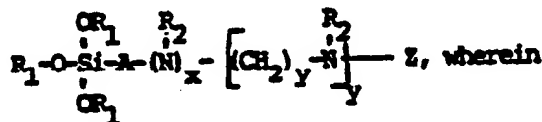
Solutions of polyimide precursors such as polyamic acids form hardened coatings by heating to high temperatures e.g., 300 to 400° C, by which the polyamic acid is imidized and solvent is removed therefrom. Similarly, soluble polyimides form hardened coatings by heating to remove the solvent.

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Aminosilane Compound:

The aminosilane compounds which are useful in the invention are those corresponding to the structural
45 formula:

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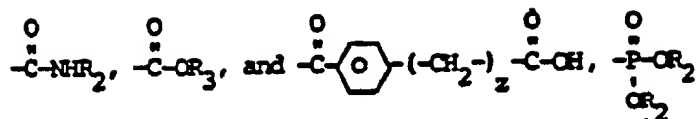


R₁ is independently selected from C₁₋₃ alkyl groups;

55 A is either phenylene or -(CH₂)_w in which w is an integer of from 1 to 6;

R₂ is independently selected from -H and C₁₋₃ alkyl groups;

Z is independently selected from -H, C₁₋₈ alkyl, C₇₋₁₂ alkaryl, C₇₋₁₂ aralkyl, glycidyl,



in which R_3 is phenyl or C_{1-8} alkyl;

x is zero or 1;

y is zero or an integer of from 1 to 3; and

z is zero or an integer of from 1 to 3;

the sum of the carbon atoms in moieties R_2 and Z being at least 3.

Among the extensive possible variations in the above-described silane structure, the following structural variations are preferred:

Moiety	Preferred Range or Composition
R_1	C_2 alkyl
A	$-(\text{CH}_2-)_3$
R_2	$-\text{H}$
x	1
y	0
z	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NHR}_2 \text{ or} \end{array}$
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OR}_3 \text{ in which} \\ R_3 = C_2 \text{ alkyl} \end{array}$

Particularly preferred aminosilane compounds for use in the invention are N-(triethoxysilylpropyl) urea and triethoxysilylpropylethylcarbamate.

The amount of aminosilane compounds which should be used in the compositions of the invention is dependent upon the amount of polyimide. It has been found that the weight ratio of the aminosilane compound to polyimide should be at least 0.01 and preferably 0.02. On the other hand, the properties of the polyimide may be degraded when too high concentrations of aminosilane are used. It is therefore preferred that the weight ratio of amino silane to polyimide not exceed about 0.2. A particularly appropriate range of concentration is 0.02-0.1.

Mixtures of aminosilane compounds falling within the above structural definition can, of course, be used. The above-described aminosilanes may also be diluted with other aminosilane adhesion promoters, such as those disclosed in the prior art, so long as the ratio of component (b) to component (a) is within the above prescribed limits.

Substrate:

The benefits of the invention in improving the adhesion of polyimide coatings is obtained on a wide variety of substrates including silicon, silica, silicon nitride, alumina and on aluminum metal as well.

Test Procedures

Adhesion:

In the examples below, the composition of the invention were tested as to substrate adhesion by spin coating onto the substrate in question a thin layer of the coating composition. The coated substrate is then heated to 350 °C to remove solvent and, in the case of polyamic acids, to convert the coatings to the polyimide form. In some instances, the coated substrate is first tested as to coating adhesion under dry conditions and in other instances it is tested after prolonged exposure to boiling water. The adhesion test is done in accordance with the procedure of ASTM D3359-83.

The invention can be better understood by reference to the following examples.

EXAMPLES

Example 1 - Preparation of Polyamic Acid

The polyamic acid was prepared by adding 10.0 grams (0.05 mole) of oxydianiline and 5.4 grams (0.05 mole) of metaphenylene diamine to 203 grams of N-methyl pyrrolidone (NMP) in a 500 ml three-neck flask equipped with a mechanical stirrer. The mixture was stirred at room temperature until all the diamine was dissolved. To this solution 32.2 grams (0.10 mole) of 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) was added slowly over 30 minutes. The reaction temperature was maintained below 40 °C for 2 hours. The resulting solution was filtered prior to use.

Examples 2-4 - Comparative Adhesion Tests

Three separate samples of the polyamic acid solution of Example 1 were used to determine the relative adhesion of the coatings of the invention to a 3-inch round silicon substrate. To one sample was added N-(triethoxysilylpropyl)urea (TSPU) in a weight ratio of 0.02 with respect to the polymer content of the polyimide solution. To a second sample was added triethoxysilylpropylamino maleic acid in the same weight ratio. Each of the two solutions and a third sample of the polyimide solution containing no adhesive promoter was spin-coated on a silicon substrate and hardened by heating to 300-400 °C. The coated substrate was then soaked in boiling water and tested as to adhesion by the procedure described above. The data for these tests are given in Table 1 below:

Table 1

Comparative Adhesion Tests			
Example No.	Adhesion Promoter	Soaking Time	Adhesion ⁽¹⁾
2	None	2	1
3	Triethoxysilylpropylamino maleic acid	88	1
4	N-(triethoxysilylpropyl)urea (TSPU)	88	5

⁽¹⁾5 = Excellent; 4 = Very Good; 3 = Good-No Adhesion Lost; 2 = Partial Failure; 1 = Failure.

These data show that the use of the prior art silane material (Example 3) was more effective than using no adhesion promoter at all. Nevertheless, the prior art material was relatively ineffective as compared to the compositions of the invention, which retained excellent adhesion even after 88 hours soaking in boiling water.

Examples 5-7 - Thermal Stability

Coated wafer samples identical to those of Examples 2-4 were subjected to thermogravimetric analysis (TGA) to observe whether the addition of the silane compounds resulted in any thermal destabilization of the polyimide. The data from these tests, which are given in Table 2 below, indicate that neither the silane used by applicants nor the silane used by the prior art caused any significant destabilization of the polyimide.

TABLE 2

Thermal Stability Measured by TGA					
Example No.	Adhesion Promoter	% Weight Retained at Temperature ⁽²⁾			
		500 ° C	525 ° C	550 ° C	575 ° C
5	None	96	94	92	86
6	Triethoxysilylpropyl amino maleic acid	96	94	91	84
7	N-(triethoxysilylpropyl) urea	96	97	91	88

⁽²⁾While heating at 10 ° C per minute.

Examples 8-11 - Adhesion to Different Substrates

The composition of Examples 4 and 7 containing 2% by weight TSPU was applied by spin coating to a number of 3-inch round wafer substrates made from different commonly used substrate materials. The data from these tests indicate that the composition of the invention was comparably effective on all four of the substrates tested.

TABLE 3

Adhesion to Various Substrates			
Example No.	Substrate Materials	Adhesion ⁽³⁾	
		No Boiling Water	72 Hours Boiling Water
8	Silicon	5	5
9	Silica	5	5
10	Silicon Nitride	5	5
11	Aluminum	5	5

⁽³⁾5 = Excellent; 4 = Very Good; 3 = Good-No Adhesion Lost; 2 = Partial Failure; 1 = Failure.

Examples 12-14 - Polyimide Variations

A further series of three polyimide solutions containing 2% wt. TSPU as an adhesive promoter was prepared in the manner described above to determine whether the effectiveness of the compositions of the invention is comparable for different polyimides. The three polyimides used can be characterized as follows:

Example 12

Same as Example 1

Example 13

PI-2590, a pre-imidized polyimide from E. I. du Pont de Nemours & Company, Wilmington, DE

Example 14

PD-2702, a photopolymerizable polyamide ester from E. I. du Pont de Nemours & Co., Wilmington, DE

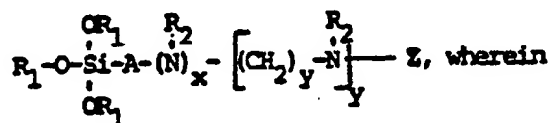
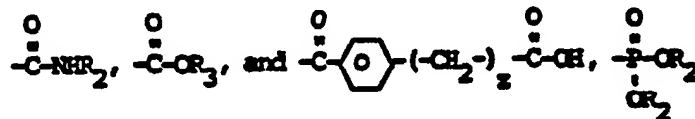
The above-described three coating solutions were spin-coated onto a 3-inch round silicon wafer and hardened at 350 °C, after which they were adhesion tested after soaking in boiling water for 88 hours. The coatings of Examples 12 and 13 both had adhesion ratings of 5, and the coating of Example 14 had an adhesion rating of 4. From these data, it is evident that the compositions of the invention are effective with a wide variety of polyimide-type coating materials.

Claims

1. A coating composition comprising an homogeneous liquid solution of:

(a) polyimide or polyimide precursor;

(b) aminosilane compound corresponding to the structural formula:

R₁ is independently selected from C₁₋₃ alkyl groups;A is either phenylene or -(CH₂)_w in which w is an integer of from 1 to 6;R₂ is independently selected from -H and C₁₋₃ alkyl groups;Z is independently selected from -H, C₁₋₈ alkyl, C₇₋₁₂ alkaryl, C₇₋₁₂ aralkyl, glycidyl, aromatic carboxyl,in which R₃ is phenyl or C₁₋₈ alkyl;

x is zero or 1;

y is zero or an integer of from 1 to 3; and

z is zero or an integer of from 1 to 3;

the sum of the carbon atoms in moieties R₂ and Z being at least 3; and

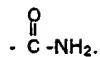
(c) aprotic solvent, the weight ratio of (b) to (a) being from 0.01 to 0.2.

2. The composition of claim 1 in which R₁ is C₂ alkyl.3. The composition of claim 1 in which A is -(CH₂)₃.4. The composition of claim 1 in which R₂ is -H.

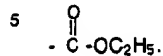
5. The composition of claim 1 in which x is 1.

6. The composition of claim 1 in which y is zero.

7. The composition of claim 1 in which Z is



8. The composition of claim 1 in which Z is



9. The composition of claim 1 in which the solvent is N-methyl pyrrolidone.

10. The composition of claim 1 in which the weight ratio of (b) to (a) is 0.02-0.1.

11. An electronic component comprising an inorganic substrate having an electronic device mounted thereon which is coated by a polymeric film formed by applying thereto a coating of the composition of claim 1 and heating the applied coating to remove solvent therefrom.

12. The component of claim 11 in which the polymer component of the coating is a polyamic acid which is dehydrated during the heating step to form the corresponding polyimide.

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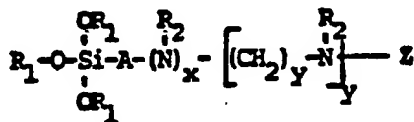
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(54) Polyimide coating composition.

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EUROPEAN SEARCH REPORT

Application Number

EP 88 11 3316

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 184 937 (HITACHI CHEMICAL CO., LTD) ---		H 01 B 3/30 H 01 L 23/28 H 01 G 4/18 H 05 K 3/28 C 09 D 3/10 C 08 L 79/08
A	EP-A-0 151 801 (IBM CORP.) ---		
D,A	US-A-4 200 724 (R. DARMS et al.) ---		
A	IEEE TRANSACTIONS ON COMPONENTS, HYBRIDS, AND MANUFACTURING TECHNOLOGY, vol. CHMT-9, no. 4, December 1986, pages 364-369, New York, US; H.R. ANDERSON et al.: "Polyimide-substrate bonding studies using gamma-APS coupling agent" -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 K C 08 L H 01 B C 09 D H 01 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-10-1990	Examiner PAULSSON R.L.
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